

REPORT DOCUMENTATION PAGE				Form Approved OMB NO. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE		3. DATES COVERED (From - To)	
		Old Reprint		-	
4. TITLE AND SUBTITLE Effect of substitution (Ta, Al, Ga) on the conductivity of Li7La3Zr2O12				5a. CONTRACT NUMBER	
				W911NF-09-1-0451	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
				611102	
6. AUTHORS J.L. Allen, J. Wolfenstine, E. Rangasamy, J. Sakamoto				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES				8. PERFORMING ORGANIZATION REPORT NUMBER	
Michigan State University Hannah Administration Building 426 Auditorium Road, Room 301 East Lansing, MI 48824 -2612					
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSOR/MONITOR'S ACRONYM(S) ARO	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) 57230-CH.17	
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT Cubic garnets of composition Li6.75La3Zr1.75Ta0.25O12, Li6.15La3Zr1.75Ta0.25Al0.2O12, and Li6.15La3Zr1.75Ta0.25Ga0.2O12 were prepared from a co-precipitated precursor and consolidated by hotpressing to a relative density of 796–98%. The total Li-ion conductivities at 298 K and activation energies (in parentheses) of Li6.75La3Zr1.75Ta0.25O12, Li6.15La3Zr1.75Ta0.25Al0.2O12 and					
15. SUBJECT TERMS Garnet, Li, Ta, Cubic, Ionic conductivity, Hot-pressing					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Lawrence Drzal
UU	UU	UU	UU		19b. TELEPHONE NUMBER
					517-353-7759

Report Title

Effect of substitution (Ta, Al, Ga) on the conductivity of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

ABSTRACT

Cubic garnets of composition $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$, $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$, and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.2}\text{O}_{12}$ were prepared from a co-precipitated precursor and consolidated by hotpressing to a relative density of 96–98%. The total Li-ion conductivities at 298 K and activation energies (in parentheses) of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$, $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$ and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.2}\text{O}_{12}$ were 0.87 mS cm^{-1} (0.22 eV), 0.37 mS cm^{-1} (0.30 eV) and 0.41 mS cm^{-1} (0.27 eV), respectively. The above results suggest that cubic stabilizing substitutions outside of the Li-ion sub-lattice are preferable to obtain faster Li-ion conductivity.

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Continuation for Block 13

ARO Report Number 57230.17-CH

Effect of substitution (Ta, Al, Ga) on the conduct ...

Block 13: Supplementary Note

© 2012 . Published in Journal of Power Sources, Vol. Ed. 0 206, (0) (2012), (, (0). DoD Components reserve a royalty-free, nonexclusive and irrevocable right to reproduce, publish, or otherwise use the work for Federal purposes, and to authroize others to do so (DODGARS §32.36). The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

Approved for public release; distribution is unlimited.



Short communication

Effect of substitution (Ta, Al, Ga) on the conductivity of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ J.L. Allen^{a,*}, J. Wolfenstine^a, E. Rangasamy^b, J. Sakamoto^b^a US Army Research Laboratory, RDRL-SED-C, 2800 Powder Mill Road, Adelphi, MD 20783, United States^b Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, United States

ARTICLE INFO

Article history:

Received 27 December 2011

Received in revised form 18 January 2012

Accepted 21 January 2012

Available online 30 January 2012

Keywords:

Garnet

Li

Ta

Cubic

Ionic conductivity

Hot-pressing

ABSTRACT

Cubic garnets of composition $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$, $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$, and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.2}\text{O}_{12}$ were prepared from a co-precipitated precursor and consolidated by hot-pressing to a relative density of ~96–98%. The total Li-ion conductivities at 298 K and activation energies (in parentheses) of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$, $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$ and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.2}\text{O}_{12}$ were 0.87 mS cm^{-1} (0.22 eV), 0.37 mS cm^{-1} (0.30 eV) and 0.41 mS cm^{-1} (0.27 eV), respectively. The above results suggest that cubic stabilizing substitutions outside of the Li-ion sub-lattice are preferable to obtain faster Li-ion conductivity.

Published by Elsevier B.V.

1. Introduction

Li-ion solid electrolytes have been long sought after in order to obtain a safe, reliable, long-lived battery system without use of flammable, volatile and relatively unstable organic liquid-based electrolytes. The advantages are numerous including long shelf life, ability to operate at high voltage or high temperature and ease of manufacturing. However, solid electrolytes have not been able to provide sufficient conductivity and/or have been unstable to Li, air or moisture. The Li-stuffed Al-substituted cubic garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) is a promising fast Li-ion conducting ceramic electrolyte owing to its fast ionic conductivity ($\sigma_{\text{total}} \sim 0.2 \text{ mS cm}^{-1}$ at 298 K) and Li and moisture stability [1,2]. High voltage Li-ion cathodes [3] that increase the demands on flammable, liquid organic electrolytes for high voltage stability [4] and safety considerations make a solid state electrolyte an attractive option. Furthermore, Li-air or Li-S batteries [5] can be enabled by the discovery and development of faster Li-ion conducting solids.

The challenge has been to stabilize the cubic form since LLZO can also exist with a tetragonal garnet structure [6,7] of lower Li-ion conductivity. The tetragonal structure results from ordering of the Li-ion sub-lattice. The first approach to stabilization of the cubic form was the serendipitous discovery that the inclusion of Al as an impurity from contamination during processing [2,7] stabilized the higher conducting cubic phase. Later Al was intentionally added

[8–11] and a dense (relative density > 90%) material with a cubic structure was obtained. Geiger et al. [7] have suggested that Al substitutes for Li and thereby stabilizes the cubic phase relative to the tetragonal phase. An Al substitution for Li will lead to a reduction in Li content in order to maintain electro-neutrality ($1\text{Al}^{3+} = 3\text{Li}^{+}$). Others have speculated that Al addition yields a denser material by acting as a sintering aid [9,10]. A similar stabilization of cubic phase is observed with Ga substitution [12]. Thus it is desirable to look at other substitutions which like the Geiger et al. approach may stabilize the cubic garnet structure through a reduction in Li content and/or increased Li vacancy concentration. Ta substitution for Zr follows this approach and it is desirable for a couple reasons. First, Ta is stable relative to Li [13]. Second, Ta substitution on the Zr site will not hinder Li-ion motion whereas Al substitution on Li sites will (as discussed later). Li et al. [13] recently reported $\text{Li}_6\text{La}_3\text{ZrTaO}_{12}$ cubic garnet with relatively high total Li-ion conductivity (0.18 mS cm^{-1} at 298 K). The sample was prepared in an alumina crucible and contained 1.3 wt% Al. Also, Logéat et al. [14] recently reported that Al-free, Ta substitution for Zr could stabilize the cubic garnet ($\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12}$). Conductivity data was not included in their report. Similarly to Ta, Nb substitution for Zr should also lower the Li content of the LLZO and a high Li ion conductivity (0.8 mS cm^{-1} at 298 K) cubic garnet sample has been reported with Nb substitution for Zr by Ohta et al. [15]. However, Ta is preferable to Nb since Nb is not chemically stable with Li [16–18] and would change LLZO from an ionic conductor to a mixed conductor. In this paper, we have chosen a level of Ta substitution equal to the level of Nb substitution reported by Ohta et al. [15] to have the highest conductivity and lowest activation energy. It is the purpose

* Corresponding author. Tel.: +1 301 394 0291; fax: +1 301 394 0273.

E-mail addresses: jan.l.allen8.civ@mail.mil, jallen@arl.army.mil (J.L. Allen).

of this paper to report on the effects of Ta, Ta + Ga and Ta + Al substitutions in order to further the understanding of Li-ion conductivity in LLZO.

2. Experimental

$\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$, $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$ and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.2}\text{O}_{12}$ were prepared for study from a co-precipitated precursor. Li_2CO_3 , $\text{La}(\text{OH})_3$, “ $[\text{ZrO}_2]_2\cdot\text{CO}_2\cdot x\text{H}_2\text{O}$ ” (zirconium carbonate, basic hydrate; equivalent ZrO_2 content determined from thermogravimetric analysis) $\text{Al}(\text{OH})_3$ and Ga_2O_3 weighed in the desired stoichiometry were dissolved in $\sim 1.4\text{M}$ HNO_3 (aq). A 3 wt% excess of Li was used to compensate for Li volatilization during synthesis. The desired amount of TaCl_5 was first dissolved in anhydrous ethanol and then added to the acid solution. The resulting clear solution was evaporated to dryness in a microwave oven contained inside a fume hood. Evolution of NO_x was observed during this step. The dried co-precipitate was lightly ground with a mortar and pestle and pressed into a pellet using a Carver laboratory die and press. The pellet was placed on a ZrO_2 plate and heated in air at 923 K for 15 h and subsequently at 1273 K for 3–4 h. The furnace was turned off and the sample was removed.

$\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$, $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$ and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.2}\text{O}_{12}$ dense discs were prepared by hot-pressing. The powders were hot-pressed at 1323 K at 40 MPa pressure for 1 h under air. From the hot-pressed discs rectangular parallelepipeds were cut using a low-speed diamond saw for density, microstructural and electrical property measurements.

X-ray diffraction (Cu $K\alpha$ radiation) was used to characterize the phase purity of the powders and the material after hot-pressing. Lattice constants were calculated from the peak positions of the X-ray diffraction pattern using Rietveld refinement of data collected in parallel beam geometry. The bulk density of the hot-pressed samples was determined from the weight and physical dimensions. The relative density values were determined by dividing the bulk density by the theoretical density. The microstructure of the hot-pressed samples was examined on fracture surfaces using scanning electron microscopy (SEM).

AC measurements were undertaken to determine ionic conductivity as a function of temperature in the range of 298–373 K. Au was sputter coated on to the top and bottom surface of the specimens. AC impedance was measured using a Solatron 1260 Impedance Analyzer in the frequency range of 1– 10^6 Hz.

3. Results and discussion

Conventional garnets are described by the formula $\text{A}_3\text{B}_3\text{O}_{12}$ where A, B, and C have 8, 4, and 6 oxygen coordination, respectively. In a cubic stuffed garnet, La occupies A sites, Zr occupies C sites and Li occupies the B sites and additional distorted octahedral sites that are unoccupied in the conventional garnet [19]. Awaka et al. [20] label the tetrahedral B site Li1 and the distorted octahedral site Li2 and they describe the basic unit of the Li sub-lattice to be loop of Li1 and Li2 sites. The Li1 site is the only connection between loops and these junctions of the basic loop unit form the complete 3-D Li ion sub-lattice and enable fast Li-ion conduction. A very high conductivity [2] was reported for cubic “ $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ” that was later shown to be a result of Al substitution for Li [7]. We believe that Al substitution lowers the Li content and stabilizes a cubic structure as hypothesized by Geiger et al. [7]. Ga can stabilize cubic garnet in a fashion similar to Al [12]. However based on the Awaka et al. structural model of Li-stuffed cubic garnet [20], the presence of Al or Ga on the Li site will be detrimental to Li-ion conduction and we therefore focused on substitutions that are

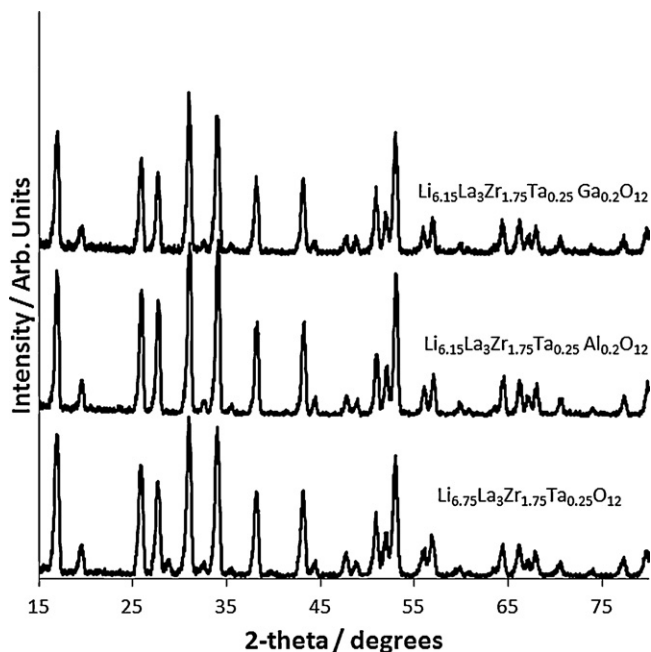


Fig. 1. The X-ray diffraction patterns of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$, $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$ and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.2}\text{O}_{12}$.

not part of the Li-ion conduction pathway. Nuclear magnetic resonance (NMR) data has shown Al occupying both the Li1 and the Li2 sites with preference for the Li1 site [7]. We speculated that Al on these sites, and in particular Al on the Li1 site, might hinder ionic conductivity since this site forms the junction between loops.

Thus, we wanted to control the Li content in order to stabilize the cubic stuffed garnet structure without placing ions such as Al or Ga on the Li sub-lattice. With this in mind, we prepared $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ where La occupies A sites, Zr and Ta occupy C sites and Li occupies B (Li1) sites as well as distorted octahedral sites (Li2) that are unoccupied in conventional garnet. We also prepared $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$ and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.2}\text{O}_{12}$ in order to determine how substitutions of Li by Ga or Al would affect the Li-ion conductivity and to shed light on the role of Ga or Al as either a substituting atom on the Li sub-lattice which reduces the Li content or as a sintering aid. Based on crystal chemistry, we expect Al to have a site preference for the tetrahedral site (B, Li1) and Ga to prefer the distorted octahedral site (Li2) [21]. We therefore expected that there may be some benefit to using Ga over Al since it may not preferentially occupy the critical Li1 junction.

The X-ray diffraction patterns for $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$, $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$ and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.2}\text{O}_{12}$ after hot-pressing are shown in Fig. 1, confirming a predominantly single phase of cubic symmetry with space group $la\bar{3}d$. From Fig. 1, it is observed that Ta does indeed stabilize the cubic LLZO phase at room temperature. The lattice parameters are shown in Table 1. By comparison, Logéat et al. [14] reports a lattice parameter of 12.96 Å for $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ which is in exact agreement with our result. Li et al. [13] reported a lattice parameter of 12.89 Å for the composition $\text{Li}_6\text{La}_3\text{ZrTaO}_{12}$. The lattice parameter change with increasing Ta content is consistent with the relative ionic radii of Ta^{5+} (64 pm) and Zr^{4+} (72 pm) [22]. Turning back to our samples, Ga or Al substitution on the Li sub-lattice has little effect on the lattice constant.

A representative micrograph of the fracture surface of the hot-pressed $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ sample is shown in Fig. 2. From SEM analysis, a couple of important points are noted. First, the material is very dense in agreement with the relative density $\sim 96\%$, determined from the physical dimensions, weight and

Table 1

Density, conductivity and lattice constants of samples prepared for this study.

Composition	Lattice constant (Å)	Relative density (%)	Total Li-ion σ at 298 K (mS cm ⁻¹)	Activation energy (eV)
Li _{6.75} La ₃ Zr _{1.75} Ta _{0.25} O ₁₂	12.96	96	0.87	0.22
Li _{6.15} La ₃ Zr _{1.75} Ta _{0.25} Al _{0.2} O ₁₂	12.95	98	0.37	0.30
Li _{6.15} La ₃ Zr _{1.75} Ta _{0.25} Ga _{0.2} O ₁₂	12.95	98	0.41	0.27

the theoretical density. Almost no porosity is observable. A high relative density is extremely important for device applications. Second, no second phases were observed at grain boundaries. Third, the fracture surface is very flat indicating transgranular fracture, revealing high grain boundary strength which should lead to low inter-granular ionic resistance. The Li_{6.15}La₃Zr_{1.75}Ta_{0.25}Al_{0.2}O₁₂ and Li_{6.15}La₃Zr_{1.75}Ta_{0.25}Ga_{0.2}O₁₂ samples also have near theoretical density (see Table 1) and exhibit microstructures similar to that shown in Fig. 2 in that very little porosity is observed and the fracture surface is very flat. In contrast the microstructure of the only other Ta-substituted LLZO material, Li₆La₃ZrTaO₁₂ [13], consolidated by conventional sintering revealed a higher percentage of intergranular fracture, which reveals that the grain boundaries are not as strong as for the present study. This should lead to a higher inter-granular resistance compared to the hot-pressed samples used in the present study. In addition, the microstructure of cubic LLZO without Ta consolidated by conventional sintering [9,10,23,24] tends to reveal a higher percentage of intergranular fracture when compared to the present hot-pressed materials which should also result in a higher inter-granular resistance.

In a device, the total Li-ion conductivity rather than bulk Li-ion conductivity is the important measure for practical application and so we will focus on total Li-ion conductivity. Furthermore, our samples because of their desirable, high density and negligible grain-boundary impedance have a total ionic conductivity nearly equal to their lattice conductivity. This point is illustrated by the room temperature Nyquist plots of all 3 samples (Fig. 3) which revealed only a nearly straight line at a slope of $\sim 45^\circ$ without any clear semi-circles. Since we used Au Li-ion blocking electrodes, the shape of the curve represents a material which is a pure Li-ion conductor. The lack of clear semi-circles at the highest frequencies is

characteristic of a material with low grain boundary impedance. This is in agreement with the results of Kotobuki et al. [9] who suggested that the lack of clear semicircles at the highest frequencies in their impedance plots implied that grain boundary impedance is negligible compared to lattice impedance and Kumazaki et al. [8] who suggested that the lack of a clear semicircle in the highest conductivity sample reveals almost complete removal of the sample grain boundary resistance.

Fig. 4 shows the Arrhenius plot of the total Li-ion conductivity of Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂, Li_{6.15}La₃Zr_{1.75}Ta_{0.25}Al_{0.2}O₁₂ and Li_{6.15}La₃Zr_{1.75}Ta_{0.25}Ga_{0.2}O₁₂ as a function of temperature. The activation energy was estimated from the slope of the line in the temperature range of 298–373 K. From Fig. 4, several important points can be made. First, the total Li-ion conductivity of Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂ is highest at all temperatures. Second, the activation energy (0.22 eV) for the total Li-ion conductivity of Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂ is considerably lower than the other two samples (0.30 eV for Li_{6.15}La₃Zr_{1.75}Ta_{0.25}Al_{0.2}O₁₂ and 0.27 eV for Li_{6.15}La₃Zr_{1.75}Ta_{0.25}Ga_{0.2}O₁₂). It is also lower than the other reported Ta-substituted LLZO garnet fast lithium-ion conductors Li₆La₃ZrTaO₁₂ (0.42 eV) [13] and lower than that reported for (Al-substituted) Li_{7-x}La₃Zr₂O₁₂ (0.30 eV) [2] and Li_{6.75}La₃Zr_{1.75}Nb_{0.25}O₁₂ (0.31 eV) [15]. Third, the conductivity of the Ga, Ta substituted sample is roughly the same as the Al, Ta substituted sample. Fourth, the activation energy of the Ga, Ta substituted sample is slightly lower than that of the Al, Ta substituted sample. Understanding the slight difference in activation energy between Ga, Ta-substituted LLZO and Al, Ta substituted LLZO is difficult owing to the small difference in activation energy. First, the two materials have very similar or equal densities, lattice constants, grain size, charge of the substituting atoms (Ta⁵⁺ and Al³⁺ or Ga³⁺)

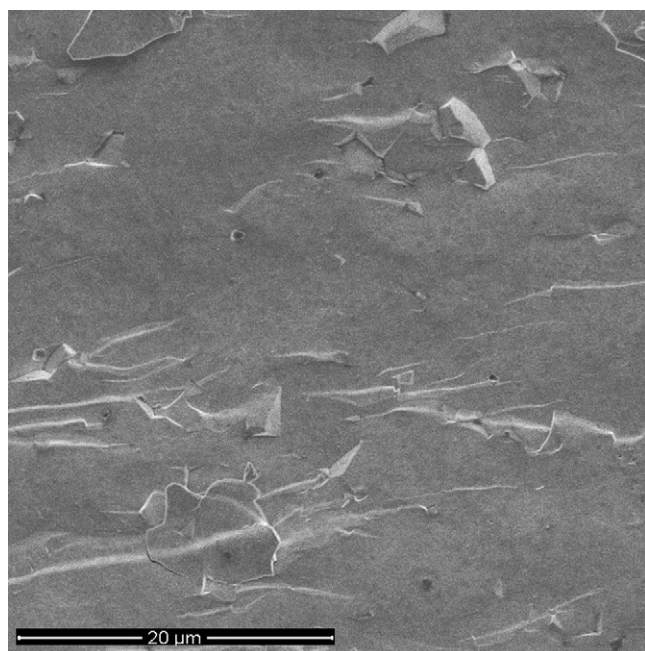


Fig. 2. Representative SEM image of a fracture surface of hot-pressed Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂.

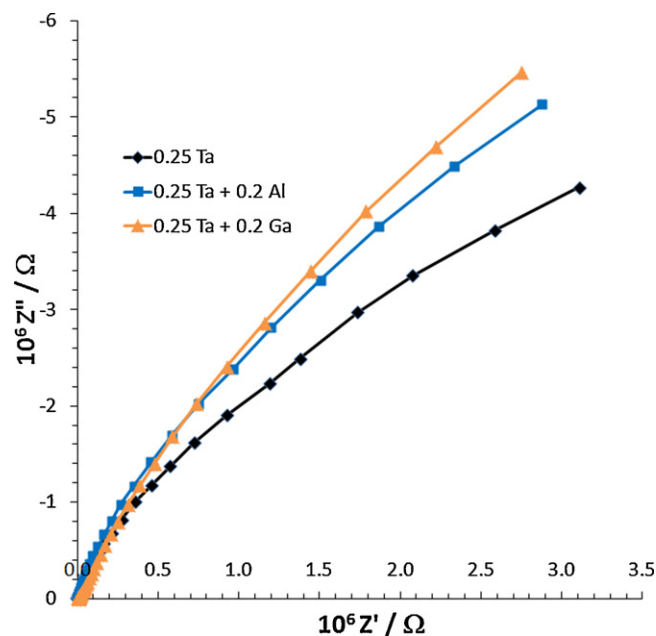


Fig. 3. Nyquist plots of the ac impedance spectra for hot-pressed samples of Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂, Li_{6.15}La₃Zr_{1.75}Ta_{0.25}Al_{0.2}O₁₂ and Li_{6.15}La₃Zr_{1.75}Ta_{0.25}Ga_{0.2}O₁₂ with Li-blocking Au electrodes at 298 K in air.

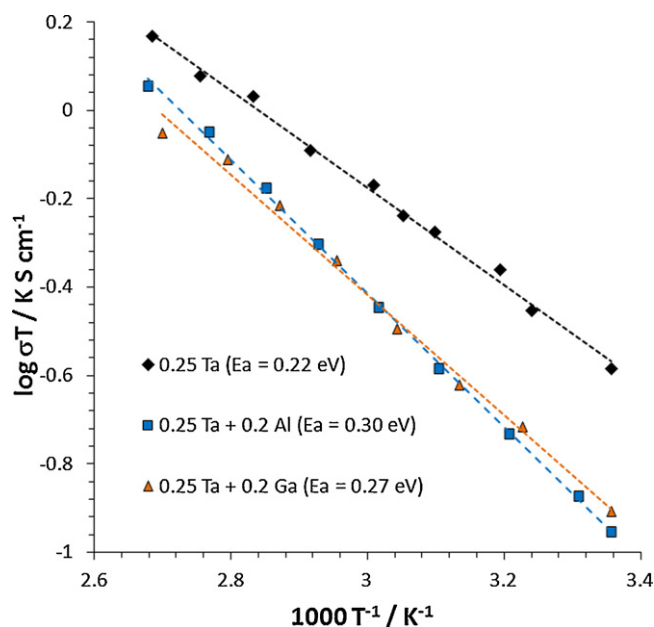


Fig. 4. Conductivity of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$, $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$ and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.2}\text{O}_{12}$ as a function of temperature.

and Li content. The only difference is the size of Al^{3+} relative to Ga^{3+} which in turn leads to different site preferences in garnets [21]. The trend is in agreement with the supposition that Ga would prefer to occupy the distorted octahedral Li2 site and Al the tetrahedral Li1 site, as discussed earlier. However, the small differences in conductivities and activation energies imply that most likely Al and Ga occupy both sites, though perhaps with a higher concentration of Ga on Li2 relative to Ga on Li1 and a higher concentration of Al on Li1 relative to Al on Li2.

Table 1 summarizes the data for all samples. Since our samples are of similar, high density (~96–98%) a good relative comparison of the effect of substitutions is possible. A couple important points can be made. First, as discussed for Fig. 4, the Ta substitution for Zr without Al or Ga leads to the highest conductivity (0.87 mS cm^{-1} at 298 K) and a very low activation energy (0.22 eV). Second, the results in Table 1 provide confirmation of the hypothesis that substitution within the Li sub-lattice by Al or Ga would be detrimental owing to its hindrance of the Li-ion conduction path. As discussed by Ohta et al. [15], the Li-ion conductivity is a function of the Li-ion concentration and the Li-ion mobility. The calculation of the Li-ion concentration difference between $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Al}_{0.2}\text{O}_{12}$ and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$ and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.2}\text{O}_{12}$ analyzed via the method of Ohta et al. [15] shows that the Li concentrations of $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$ and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.2}\text{O}_{12}$ are 90% of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$. This 10% difference in Li-ion concentration cannot explain the >2-fold increase in conductivity. Therefore, the Li-ion mobility difference is the predominant factor which controls the conductivity difference. This is further supported by the lower activation energy of $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ (0.22 eV) relative to $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$ (0.30 eV) and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.2}\text{O}_{12}$ (0.27 eV). Al or Ga on the Li sub-lattice hinders the Li-ion mobility. Third, at least for hot pressing, Al or Ga substitution is not needed in order to obtain a sample with high density and fast Li-ion conductivity.

By way of comparison, Li et al. [13] reported a total Li-ion conductivity at 298 K of 0.18 mS cm^{-1} for the Ta-substituted LLZO garnet of composition $\text{Li}_6\text{La}_3\text{ZrTaO}_{12}$. Al was also found in the sample at a weight percent of 1.3 which is about 0.4 M or about twice as much as our Al-containing sample. This is the only other reported

conductivity for Ta-substituted LLZO however the comparison is not ideal since we do not know the density of the Li et al. sample and the Ta content and Al content is different. In contrast, our Ta, Al substituted sample ($\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$) had a conductivity of $\sim 0.37 \text{ mS cm}^{-1}$. Qualitatively, we can say that first, the lower conductivity of the Li et al. [13] sample may result from lower sample density and the higher Al (reduced Li-ion mobility) and Ta content (reduced Li-ion concentration). Second, the activation energy of the Li et al. sample is considerably higher (0.42 eV) which is probably a result of higher grain boundary resistance as well as some blockage of the Li sub-lattice by the higher content of Al.

Also, as comparison, the total Li-ion conductivity and activation energy of our sample of composition $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ (0.87 mS cm^{-1} and 0.22 eV) can be compared to the Nb-substituted LLZO of composition, $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ (0.8 mS cm^{-1} and 0.31 eV) [15]. The conductivity values are in excellent agreement. The activation energy of our sample is lower as a result of the higher relative density (96%) obtained via hot-pressing relative to sintering (89–92%). These values approach the calculated (via molecular dynamics simulation) bulk lattice conductivity of 1 mS cm^{-1} reported by Adams et al. [25].

Turning once again to our samples, these results support the supposition that high ionic conductivity can be achieved by Ta substitution for Zr cubic garnet stabilizing substitutions that do not place the substituting atom (Al or Ga) in the conductive pathway of Li. Both Nb [15] and Ta (this work) substituted LLZO exhibited higher conductivity than Al-substituted LLZO [2]. Ta is preferred owing to its higher stability against Li reduction.

4. Conclusion

Cubic LLZO can be stabilized at room temperature by the addition of Ta. Hot-pressed $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$, $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$ and $\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.2}\text{O}_{12}$ have a relative density of ~96–98%. The room temperature AC conductivity results for the hot-pressed $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ sample yields a total ionic conductivity value $\sim 0.87 \text{ mS cm}^{-1}$ and activation energy of 0.22 eV. Addition of Al or Ga to Ta-substituted LLZO reduces the conductivity and increased the activation energy suggesting that Al or Ga substitutions in the Li-ion sub-lattice tend to lower the Li-ion conductivity.

Acknowledgments

J.L.A. and J.W. would like to acknowledge support of the US Army Research Laboratory (ARL). E.R. and J.S. authors would like to acknowledge the support of the US Army Research Office (ARO).

References

- [1] Y. Shimonishi, A. Toda, T. Zhang, A. Hirano, N. Imanishi, O. Yamamoto, Y. Takeda, *Solid State Ionics* 183 (2011) 48.
- [2] R. Murugan, V. Thangadurai, W. Weppner, *Angew. Chem. Int. Ed.* 46 (2007) 7778.
- [3] J.L. Allen, T.R. Jow, J. Wolfenstine, *J. Power Sources* 196 (2011) 8656.
- [4] A. von Cresce, K. Xu, *Electrochem. Solid State Lett.* 158 (2011) A337.
- [5] P.G. Bruce, L.J. Hardwick, K.M. Abraham, *MRS Bull.* 36 (2011) 506.
- [6] J. Awaka, N. Kijami, H. Hayakawa, J. Akimoto, *J. Solid State Chem.* 182 (2009) 2046.
- [7] C.A. Geiger, E. Alekseev, B. Lazic, M. Fisch, T. Armbruster, R. Langner, M. Fechtelkord, N. Kim, T. Pettke, W. Weppner, *Inorgan. Chem.* 50 (2011) 1089.
- [8] S. Kumazaki, Y. Iriyama, K.-H. Kim, R. Murugan, K. Tanabe, K. Yamamoto, T. Hirayama, R. Murugan, Z. Ogumi, *Electrochem. Commun.* 13 (2011) 509.
- [9] M. Kotobuki, H. Munakata, K. Kanamura, Y. Sato, T. Yoshida, *J. Power Sources* 196 (2011) 7750.
- [10] Y. Jin, P.J. McGinn, *J. Power Sources* 196 (2011) 8683.
- [11] E. Rangasamy, J. Wolfenstine, J. Sakamoto, *Solid State Ionics* 206 (2012) 28.
- [12] J. Wolfenstine, J. Ratchford, E. Rangasamy, J. Sakamoto, J.L. Allen, *Mater. Chem. Phys.*, under review.
- [13] Y. Li, C.-A. Wang, H. Xie, J. Cheng, J.B. Goodenough, *Electrochem. Commun.* 13 (2011) 1289.

- [14] A. Logéat, T. Kohler, U. Eisele, B. Stiaszny, A. Harzer, M. Tovar, A. Senyshyn, H. Ehrenberg, B. Kozinsky, *Solid State Ionics* 206 (2012) 33.
- [15] S. Ohta, T. Kobayashi, T. Asaoka, *J. Power Sources* 196 (2011) 3342.
- [16] N. Kumagai, N. Ikenoya, I. Ishiyama, K. Tanno, *Solid State Ionics* 28 (1998) 862.
- [17] Y. Li, C. Sun, J.B. Goodenough, *Chem. Mater.* 23 (2011) 2292.
- [18] J.M. Amarilla, B. Casal, E. Ruiz-Hitzky, *J. Mater. Chem.* 6 (1996) 1005.
- [19] E.J. Cussen, T.W.S. Yip, G. O'Neill, M.P. O'Callaghan, *J. Solid State Chem.* 184 (2011) 470.
- [20] J. Awaka, A. Takashima, K. Kataoka, N. Kijima, Y. Idemoto, J. Akimoto, *Chem. Lett.* 40 (2011) 60.
- [21] S. Geller, *Z. Kristallogr.* 125 (1967) 1.
- [22] R.D. Shannon, *Acta Crystallogr. A* 32 (1976) 751.
- [23] J. Tian, A. Tiwari, *Electrochem. Solid State Lett.* 15 (2012) A37.
- [24] M. Huang, T. Liu, Y. Deng, H. Geng, Y. Shen, Y. Lin, C.-W. Nan, *Solid State Ionics* 204–205 (2011) 41.
- [25] S. Adams, P.R. Rayavarapu, *J. Mater. Chem.* 22 (2012) 1426.